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Highly selective synthesis of 2,6-dimethylnaphthalene over alkaline treated ZSM-12 zeolite

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Abstract

ZSM-12 zeolites synthesized by using different templates were modified by desilication treatment in alkaline medium. The samples before and after alkaline treatment were characterized by X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), N_2 physical adsorption, solid state NMR (^{29}Si MAS NMR), ammonia temperature programmed desorption (NH_3-TPD) and FT-IR spectroscopy of adsorbed pyridine (Py-IR). The effects of desilication on the structure, acidity and catalytic performance in the alkylation of naphthalene with methanol over ZSM-12 zeolites were investigated. The results showed that acidity of ZSM-12 zeolites could be adjusted and mesopores were generated after alkaline treatment, so catalytic performance was effectively improved, and increase of naphthalene conversion, selectivity to 2,6-DMN and 2,6-/2,7-DMN ratio were observed over the alkaline treated samples.

Keywords: ZSM-12 zeolite; 2,6-dimethylnaphthalene; Desilication; Alkylation

1. Introduction

Synthesis of 2,6-dimethylnaphthalene (2,6-DMN), as a preferred monomer for high-performance polymeric materials such as polyethylenenaphthelene (PEN) has aroused more attention. Compared with

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other thermoplastic polyesters (e.g., polyethylene terephthalate, PET), PEN has improved thermal, mechanical and gas barrier properties that render it suitable to several applications [1-4]. To date, 2,6-DMN is produced at large scale (30 kton/year) only by BP-Amoco. The employed process is quite complex, since it involves four subsequent reaction steps starting from o-xylene and butadiene. With a view to reduce the cost of 2,6-DMN production, alternative processes for the synthesis of this substance have also been investigated. Among them, alkylation of naphthalene (NAPH) with methanol is a potentially attractive reaction to obtain 2,6-DMN [5-8]. But methylation of NAPH is a complicated reaction, and the reaction products are a mixture of ten dimethylnaphthalenes isomers which have similar molecular dimensions and thermodynamic properties. Especially, since 2,6-DMN and 2,7-DMN have almost the same boiling point, it is difficult to separate them. So developing a new catalyst which has excellent catalytic performance and selectivity to 2,6-DMN is the key to this reaction.

Millini investigated energy barriers (ΔE) for the diffusion of reactants and products over ZSM-12, MFI, MOR and BEA. The result showed that in almost all the examined zeolites, the ΔE values computed for 2,6-DMN and 2,7-DMN were very similar and the observed differences were not sufficiently high to predict relevant selectivity toward the two products. The only case where significant differences have been observed was ZSM-12. In fact, 2,6-DMN was predicted to diffuse substantially unhindered in the puckered 12-MR channels of the ZSM-12 zeolite, while the 2,7-DMN was not (ΔE= 10.9 and 102.6 kJ/mol, respectively) [4]. ZSM-12 zeolite has moderate acidity and one-dimensional channel system (pore diameter is 0.57×0.61 nm), so it is considered to be a suitable catalyst for alkylation of NAPH with methanol. However, the catalytic performance of ZSM-12 zeolite is compromised due to their microporous character, which often leads to intracrystalline diffusion limitations with numerous undesired effects. The performance of ZSM-12 zeolite can be improved by introduction of mesopores into the zeolite micropore networks. Mesopores ensure an optimal accessibility and transport of reactants and products, while the zeolitic micropores induce the preferred shape-selective properties. Recently, a post-treatment method, namely desilication (selective removal of framework Si from zeolite matrix) by alkaline treatment has been introduced as an effective approach for the mesopores generation and has gained significant attention. Additionally, this approach is effective for generating mesoporosity in Si rich zeolites (high Si/Al ratios), such as ZSM-12 zeolite [9]. High-performance catalyst is required for alkylation of NAPH with methanol, so alkaline treatment is used to modify ZSM-12 zeolite to improve catalytic activity and the selectivity for 2,6-DMN.

2. Experimental

Methyltriethylammonium bromide (MTEABr) and tetraethylammonium bromide (TEABr) were used as templates to synthesized ZSM-12 zeolites, respectively. Hydrothermal crystallization of the synthetic gel with a molar composition of 16.25 MTEABr (or TEABr): 1 Al_2O_3: 4.225 Na_2O: 130 SiO_2: 1690 H_2O was carried out at 160°C for 5 days. Hereinafter, the H form samples synthesized using MTEABr and TEABr were designated HZ-M and HZ-T, respectively. The samples prepared through alkaline treatment by 0.8 mol/L NaOH solution for 30 min at 65°C were denoted as HZ-M-AT and HZ-T-AT, respectively.

X-ray diffraction patterns were recorded on a Rigaku D/MAX-2400 diffractometer. Elemental analysis was carried out on a Bruker SRS3400 X-Ray Fluorescence apparatus. The nitrogen adsorption and desorption isotherms were obtained by using a Quantachrome AUTOSORB-1-MP adsorption unit. The acid properties were examined by temperature programmed desorption of NH_3 (NH_3-TPD) on a conventional apparatus with a thermal conductivity detector (TCD) and pyridine-adsorbed Fourier transform infrared (Py-IR) spectra on a PerkinElmer Spectrum100 spectrometer. ^{29}Si MAS NMR spectra were measured using Varian Infinity plus 300WB spectrometer.

The NAPH methylation was carried out in a fixed-bed, continuous-flow microreactor at 350°C under 4 MPa. The catalyst was placed in the constant temperature zone of the reactor, activated at 500°C for 1 h under N_2 flow of 70 ml/min, and then cooled down to 350°C. The liquid feed, including naphthalene, methanol and 1,2,4-trimethylbenzene in a molar ratio of 1: 2: 8, was pumped into the reaction system by a micro-metering pump simultaneously with a 10 ml/min N_2 flow. The weight hourly space velocity (WHSV) of the total reaction feed was 3 h^{-1} in all experiments. The reaction products were analyzed by gas chromatography (GC) using an Agilent 6890 GC unit equipped with a WCOT PLC capillary column (50 m×0.25 mm×0.25 μm).

3. Result and discussion

3.1. Structural properties of the parent and alkaline treated samples

XRD patterns show the reflection peaks of ZSM-12 zeolite at 2θ=8.8°, 20.6° and 22.9° before and after modification, suggesting that alkaline treatment does not destroy the MTW topological structure. As seen from Table 1, the relative crystallinity of the samples decreases to some extent after alkaline treatment, indicating that Si is removed from framework of ZSM-12 zeolite. XRF measurements show that Si/Al ratio of HZ-T-AT increases after modification, suggesting that dealumination occurs simultaneously with desilication, so among two processes dealumination is more evident [10]. The framework of HZ-M is steadier than HZ-T; some of the dissolved Si species deposit on the surface of the catalyst, so Si/Al ratio changes slightly after alkaline treatment. Considering N_2 physical adsorption data, the mesopore volume of HZ-T is larger than that of HZ-M because of larger crystal defects formed during synthesis process. If compared with HZ-M-AT sample, the mesopore volume of HZ-T-AT sample increases more significantly. Meanwhile, a hysteresis loop which is characteristic for mesoporous network is appeared in the isotherm of HZ-T-AT (Fig.1), indicating that this sample possesses more secondary mesopores. Micropore volumes and total pore volumes increase after alkaline treatment of samples, implying that amorphous and non-framework species have been dissolved in alkaline solution.

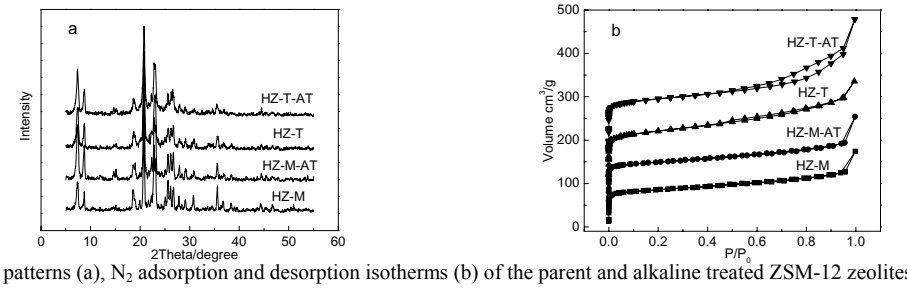

Fig.1. XRD patterns (a), N_2 adsorption and desorption isotherms (b) of the parent and alkaline treated ZSM-12 zeolites

Table 1. Physical and chemical properties of the parent and alkaline treated ZSM-12 zeolites

Samples	Surface area,m^2/g			Pore volume, cm^3/g			Relative Crystallinity (%)	Si/Al ratio[d]
	BET[a]	Micro[b]	Extern	Total[c]	Micro	Meso		
HZ-M	329	246	83	0.270	0.098	0.172	100	62
HZ-M-AT	343	251	91	0.301	0.100	0.201	98	64
HZ-T	327	239	88	0.335	0.097	0.238	100	67
HZ-T-AT	376	259	117	0.440	0.106	0.334	93	89

[a] BET method, [b] t-plot method, [c] Volume adsorbed at p/p_0 =0.99, [d]measured by XRF method

In the ^{29}Si NMR spectrum of HZ-M and HZ-M-AT samples (Fig. 2a), there are two signals with chemical shifts at -111 ppm and -102 ppm, the corresponding peak area ratio are 10.3 and 7.0,

respectively. In the ^{29}Si NMR spectrum of HZ-T and HZ-T-AT (Fig. 2b), two signals at -112 ppm and -102 ppm with a peak area ratio of 7.6 and 8.6, respectively, are observed. The signal with chemical shift at -102 ppm corresponds to Si(1Al), while signals with chemical shifts at -111 ppm and -112 ppm represent Si(0Al). The ^{29}Si NMR results indicate that desilication mainly occurs on HZ-M, while dealumination is more evident than desilication on HZ-T under the same alkaline medium.

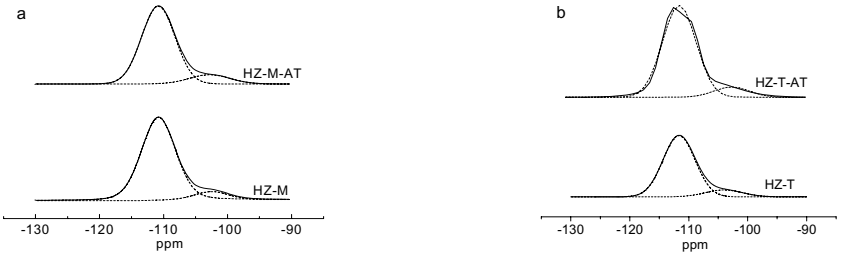

Fig.2. ^{29}Si MAS NMR spectra of the parent and alkaline treated ZSM-12 zeolites

Table 2. ^{29}Si MAS NMR data of the parent and alkaline treated ZSM-12 zeolites

Samples	Si(0Al)/Si(1Al)
HZ-M	10.3
HZ-M-AT	7.0
HZ-T	7.6
HZ-T-AT	8.6

3.2. Acidic properties of the parent and alkaline treated samples

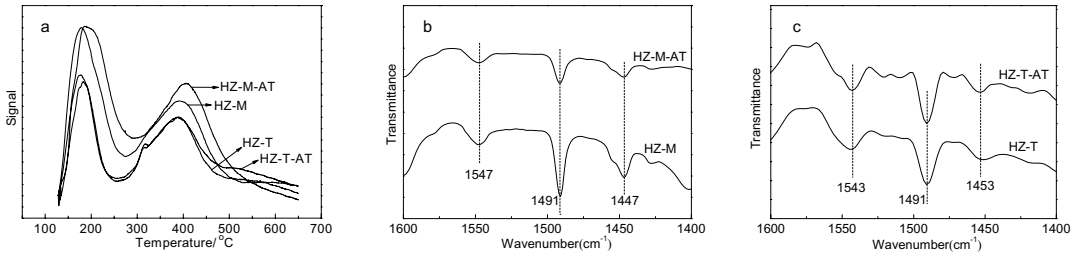

Fig.3. NH_3-TPD profiles (a) and Py-IR spectra (b, c) of the parent and alkaline treated ZSM-12 zeolites

Table 3. NH_3-TPD data of the parent and alkaline treated ZSM-12 zeolites

Samples	Temperature of NH_3 desorption (℃)		Acidity (mmol/g)[a]		
	Weak	Strong	Weak	Strong	Total
HZ-M	173	393	0.293	0.195	0.488
HZ-M-AT	188	406	0.332	0.250	0.582
HZ-T	175	390	0.195	0.145	0.340
HZ-T-AT	181	390	0.191	0.144	0.335

[a] determined by NH_3-TPD data

It can be seen from Fig 3(a) that each curve has two desorption peaks appearing at high and low temperatures, respectively, with the former assigned to strong acid sites and the later to weak acid sites. NH_3-TPD data (Table 3) show that acidic strength and acidity of HZ-M-AT increase obviously, it is caused by desilication of HZ-M which is in consistent with ^{29}Si MAS NMR result. However, acidity of HZ-T-AT decreases slightly compared with the sample HZ-T, indicating that dealumination occurs along with desilication. Fig. 3(b) and (c) show the FT-IR spectra of pyridine adsorbed on the parent and alkaline

treated ZSM-12 samples after desorption at 150°C. The relatively strong peak around 1545 cm^{-1} is attributed to pyridine bound on Brønsted acid sites; the peak at 1491 cm^{-1} is attributed to pyridine associated with both Brønsted and Lewis acid sites; a weak peak around 1450 cm^{-1} is due to pyridine bound on Lewis acid sites. According to table 4, B/L ratio of HZ-M-AT increases because of non-framework Al species are dissolved in alkaline medium, result in the decrease of Lewis acid amount. In terms of HZ-T-AT, Al species are removed after alkaline treatment, which leads to the decrease of Brønsted and Lewis acid amount, but there is no change of B/L ratio.

Table 4. Py-IR data of the parent and alkaline treated ZSM-12 zeolites

Samples	Wavenumber (cm^{-1})			Acidity (mmol/g)			B/L ratio[b]
	Brønsted	Brønsted and Lewis	Lewis	Brønsted	Lewis	Total[a]	
HZ-M	1547	1491	1447	0.235	0.253	0.488	0.9
HZ-M-AT	1547	1491	1447	0.340	0.242	0.582	1.4
HZ-T	1543	1491	1453	0.264	0.076	0.340	3.5
HZ-T-AT	1543	1491	1453	0.261	0.074	0.335	3.5

[a] determined by NH_3-TPD data

[b] determined by Py-IR data, B/L=1.5×(AB/AL)

3.3. Catalytic performance of the parent and alkaline treated samples

It can be seen from Table 5 that HZ-T exhibits better catalytic performance compared with HZ-M, which is caused by its suitable mesoporous structure despite relatively weak acidity. NAPH conversion, 2,6-DMN selectivity and 2,6/2,7-DMN ratio are higher over HZ-T-AT compared with HZ-M-AT due to the improved mesoporosity of HZ-T-AT without destroying the microporous framework of ZSM-12. Despite a slight change of acidity after alkaline treatment, the generated mesoporous structure promotes the diffusion of 2,6-DMN which possesses larger molecular dimension compared with 2,7-DMN. Additionally, selectivity towards DMN and TMN also increases after the modification because of the increased mesoporous structure. After alkaline treatment, acid strength and acidity of HZ-M-AT increase obviously, but mesopore volumes enlarge not significantly. So NAPH conversion, 2,6-DMN selectivity and 2,6/2,7-DMN ratio increase over this catalyst only by 5.27%, 2.30% and 0.29, respectively. However, HZ-T-AT possesses considerably larger mesoporous structure that effectively improves diffusion of reactants and products, so NAPH conversion, 2,6-DMN selectivity and 2,6/2,7-DMN ratio increase from 43.28%, 24.99% and 1.85 to 54.64%, 26.56% and 2.00, respectively. Taking together, we conclude that this reaction is mainly controlled by diffusion resistance.

Table 5. Effect of the parent and alkaline treated ZSM-12 zeolites on alkylation of NAPH with methanol. Reaction conditions: T=350°C, P=4 MPa, WHSV=3 h^{-1}, NAPH: CH_3OH: 1,2,4-TMB=1: 2: 8 (mol.), TOS=5 h

Samples	HZ-M	HZ-M-AT	HZ-T	HZ-T-AT
Conversion of NAPH (%)	17.39	22.66	43.28	54.64
Product selectivity (%)				
MN	85.83	79.21	65.77	57.83
DMN	13.20	17.02	28.65	34.08
TMN	0.97	3.77	5.58	8.09
DMN distribution (%)				
2,6-DMN	14.00	16.30	24.99	26.56
2,7-DMN	16.00	13.89	13.53	14.15
2,3-DMN	6.00	5.40	3.45	3.24
Others	64.00	64.41	58.03	56.05
2,6-/2,7-DMN ratio	0.88	1.17	1.85	2.00

4. Conclusion

Two ZSM-12 zeolites were successfully synthesized using MTEABr and TEABr as templates, and the prepared samples were modified with the alkaline solution. A number of physicochemical methods were used to investigate their structure, acidity and catalytic performance. After alkaline treatment, Si species were removed from the framework of HZ-M. As a result, acid strength and acidity increased, but the mesopore volumes changed slightly, so NAPH conversion and selectivity towards 2,6-DMN improved not evidently over HZ-M-AT. In terms of HZ-T-AT, dealumination of the parent zeolite occurred simultaneously with desilication during the treatment in alkaline medium. For this sample, larger mesoporous volume was formed and, despite a slightly decrease in acidity, catalytic performance of HZ-T-AT enhanced markedly. Improved NAPH conversion, 2,6-DMN selectivity and 2,6/2,7-DMN ratio were obtained over HZ-T-AT sample prepared by alkaline treatment of ZSM-12 zeolite due to its suitable acidity and mesoporosity.

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